

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.569:544.77

FORMING PROPERTIES OF BODIES FOR CASTING SANITARY WARE CERAMICS

V. G. Sal'nik,^{1,2} V. A. Sviderskii,¹ and L. P. Chernyak¹

Translated from *Steklo i Keramika*, No. 3, pp. 3 – 6, March, 2013.

The coagulation structural and technological properties of slip bodies for casting ceramics on stands in gypsum molds and under pressure in polymer molds are shown. Body compositions that optimize water systems with differentiation of casting methods and porcelain structure during firing are presented.

Key words: ceramic sanitary ware, composition, slip, casting, structure.

Currently, the manufacture of ceramics for sanitary ware requires methods for intensifying casting on mechanized stands and under pressure, which requires developing new bodies that give the appropriate filtration parameters for molding in gypsum or polymer porous molds [1 – 6]. At the same time the technological parameters of slip bodies as disperse water systems are related with their coagulation structure [7, 8]. For this reason, the compositions of bodies should be optimized, taking account of the characteristics of the raw material used and differentiating casting methods by composition – structure – properties relationships.

CHARACTERISTICS OF THE EXPERIMENTAL OBJECTS

Ceramic slip bodies MZTs₀₇ and VTs₅₀₇ for stand casting in gypsum molds and VT₀₇ for pressure casting became the objects of study. These bodies are used at the Slavutich combine Budfarfor, JSC. Some characteristics of the experimental bodies are the same and some differ widely (Tables 1 – 3).

In contrast to MZTs₀₇ and VTs₅₀₇, the VT₀₇ body contains considerably less clayey components — 50.5 versus 65.4 – 67.0%³ owing to the 1.5 times smaller amount of kaolins, more feldspar materials — 21.6 versus 12.7 – 13.4% and twice the amount of quartz sand – 20.9 versus 9.3 – 10.1%.

These differences in the quantitative ratio of clays and kaolins determine their dispersity. The clay part of the VT₀₇ body with approximately the same amount of fine particles in the 0.005 – 0.001 mm and .001 mm fractions differs by the much lower content of coarse particles from the

TABLE 1. Bodies for Casting Sanitary Ware Ceramics

Raw materials	Component content, wt.%		
	VT ₀₇	MZTs ₀₇	VTs ₅₀₇
Clay:			
Vesko-Granitik	7.0	6.0	7.0
DN-0	–	11.0	7.0
PLG-1	–	5.0	
ESBKA-2	–	–	7.0
Santon-L	15.0	–	
Kaolin:			
Glukhovetskoe KS-1	18.5	6.0	3.5
Prosyanovskoe KS-1	–	6.0	8.9
KICK-2	10.0	–	
K0-1	–	5.0	5.0
KSSK	–	26.4	28.6
Feldspar:			
Chalm-ozero KNSHM 0.2-2	3.0	5.0	5.0
Vishnevogorsk PShS 0.2-2.1	18.6	4.5	4.7
Zhitomir “mine” PT	–	3.9	3.0
Quartz sand	20.9	10.1	9.3
Porcelain fragments	7.0	11.0	11.0

¹ National Technical University of Ukraine – Kiev Polytechnic Institute, Kiev, Ukraine.

² E-mail: salnik@ubm.ua.

³ Here and below, content by weight, %.

TABLE 2. Dispersity of Clay Components of Bodies

Body	Content, wt.%, particle fractions, mm				
	1.00 – 0.06	0.06 – 0.01	0.01 – 0.005	0.005 – 0.001	>0.001
MZTs ₀₇	17.05	3.74	2.85	9.53	32.23
VTs ₅₀₇	18.25	5.42	3.74	11.06	28.52
VT ₀₇	0.48	8.43	5.34	13.66	28.86

TABLE 3. Chemical Composition of Bodies

Body	Oxide content, wt.%			
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
MZTs ₀₇	63.70	23.10	0.60	0.95
VTs ₅₀₇	63.83	23.00	0.65	0.92
VT ₀₇	64.23	22.38	0.60	0.77

Body	Oxide content, wt.%			
	MgO	Na ₂ O	K ₂ O	other
MZTs ₀₇	0.43	1.15	2.66	6.08
VTs ₅₀₇	0.42	1.10	2.76	6.08
VT ₀₇	0.19	1.77	3.00	5.74

1.00 – 0.06 mm fraction. In the clayey part of the bodies the ratio of the 1.00 – 0.0 mm and < 0.001 mm fractions drops to 0.02 in the case of VT₀₇ versus 0.53 – 0.64 for MZTs₀₇ and VTs₅₀₇.

Irrespective of the methods used to mold articles, the chemical composition of the bodies gives the required degree of sintering in a prescribed firing regime. The VT₀₇ body differs by the following:

- higher content of the total alkali oxides Na₂O + K₂O (4.77 versus 3.81 – 3.86%) and lower ratio K₂O : Na₂O (1.7 versus 2.3 – 2.5);
- lower total content of alkali-earth oxides CaO + MgO (0.96 versus 1.34 – 1.38%) with higher total content of the oxides of the type R₂O + RO (5.73 versus 5.20%).

X-ray phase analysis shows that the mineralogical composition of the experimental bodies includes quartz, feldspars (microcline, orthoclase, albite), kaolinite and hydromica.

The intensity ratios of the characteristic reflections show that the VT₀₇ body contains more quartz and orthoclase.

COAGULATION STRUCTURE OF SLIP BODIES

The modern technology of sanitary ware ceramics uses slip bodies differing by composition, properties and content of the disperse phase and by the composition and properties of the dispersion medium. The basic properties of such highly concentrated disperse systems are determined by the ratio of the potential energy of interaction (bonding) of the particles and the kinetic energy, whose sources are external mechanical actions [9].

The formation of the coagulation structure of slip bodies in the ceramic casting technology is characterized by the following stages: interaction of the surface of the particles of the disperse phase components with the dispersion medium (water + electrolytes), change of the chemical-mineralogical and granulometric compositions with additional introduction of clayey components into containers, partial destruction and change of the rheological characteristics under external pressure with transport to molds, growth of the disperse phase concentration with water withdrawal in a gypsum mold or under external pressure in a polymer mold.

The coagulation structure of slip bodies has the general characteristics of structural-mechanical and rheological properties, but it can differ considerably with respect to quantitative indicators.

A study of the deformation processes in slip bodies has shown (Tables 4 and 5) that according to the development of fast elastic ε'_0 , slow elastic ε'_2 and plastic $\varepsilon'_1\tau$ deformations the MZTs₀₇ and VTs₅₀₇ samples are of the third structural-mechanical type, for which $\varepsilon'_0 \geq \varepsilon'_1\tau > \varepsilon'_2$. However, there is a definite difference in the quantitative values and ratios of the types of deformations indicated.

For example, for approximately equal development of ε'_0 $(13.08 - 13.70) \times 10^8$ the slip body MZTs₀₇ differs from VTs₅₀₇ by half the development of ε'_2 and 1.5 times larger $\varepsilon'_1\tau$, and components 2.37×10^8 and 13.01×10^8 versus 5.96×10^8 and 8.41×10^8 , respectively.

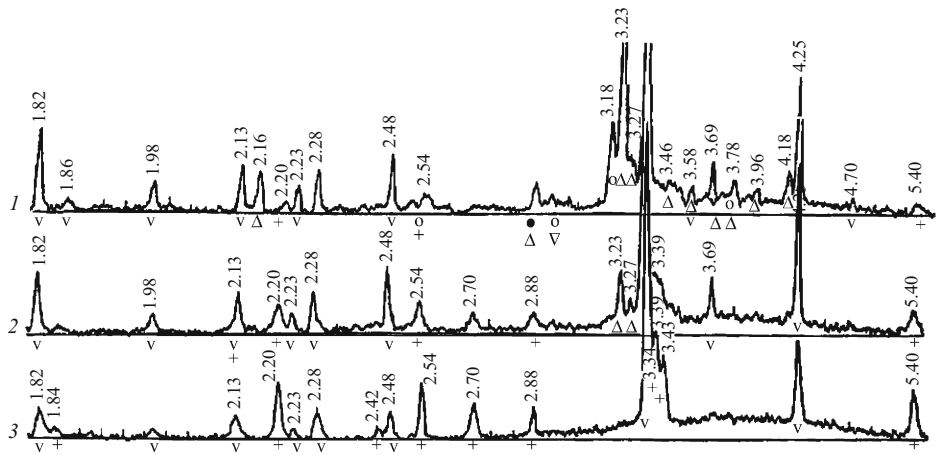
The slip body VT₀₇ is of the fourth structural-mechanical type, where $\varepsilon'_1\tau > \varepsilon'_0 > \varepsilon'_2$. It differs from MZTs₀₇ and

TABLE 4. Structural-Mechanical Characteristics of Slip Bodies

Sample	$E_1 \times 10^{-4}$, Pa	$E_2 \times 10^{-4}$, Pa	P_{k1} , Pa	$\eta_1 \times 10^{-2}$, Pa · sec	λ	$(P_{k1}/\eta_1) \times 10^2$, sec ⁻¹	θ_1 , sec	$E_\varepsilon \times 10^{-3}$, ergs/cm ³
MZTs ₀₇	1.53	8.46	23.61	15.38	0.15	1.54	1186	0.71
VTs ₅₀₇	1.46	3.36	38.92	23.78	0.30	1.64	2331	0.72
VT ₀₇	1.72	5.21	8.10	11.55	0.25	0.71	887	0.61

Notations: E_1) modulus of the fast elastic deformation; E_2) modulus of the slow elastic deformation; P_{k1}) conditional static yield stress; η_1) highest plastic viscosity; λ) elasticity; P_{k1}/η_1) static plasticity; θ_1) period of true relaxation; E_ε) constrained modulus of deformation.

Fig. 1. Diffraction patterns of ceramic from VT₀₇ body after firing at 1000°C (1), 1100°C (2) and 1220°C (3): v) quartz; +) mullite; △) microcline; ○) orthoclase; ▽) albite.



VTs₅₀₇ by a considerable development of the plastic deformation $\epsilon'_1 \tau$, which comprises 17.32×10^8 . Thus, in keeping with the physical-chemical mechanics of disperse structures, for the body MZTs₀₇ as compared with VTs₅₀₇ with approximately the same amount of the strongest corner – corner, corner – edge and edge – edge particle contacts the number of plane – corner, plane – edge and plane – plane contacts is characteristically smaller.

In the case of the body VT₀₇ the higher plastic deformation, shorter period of true relaxation and fourth structural type classification indicate higher flowability and lower kinetic stability of the slip. In addition, the higher plasticity, shorter period of true relaxation and lower stability of the slip are due to smaller effective specific surface area, larger particle size and higher perfection of the crystal structure of the monomineral components of the clayey raw material.

Irrespective of these differences in the quantitative ratios of the types of deformation the slip body VT₀₇ is characterized by lower than for MZTs₀₇ and VTs₅₀₇ constrained modulus of deformation E_e , i.e., weaker bonding forces between particles of the disperse phase.

The decrease of the viscosity η_1 and period of true relaxation θ_1 are associated to structural-mechanical factors of lower stability of clayey suspensions. Accordingly, the bodies fall into the following order according to kinetic stability: VT₀₇ < MZTs₀₇ < VTs₅₀₇.

Analysis of the rheological properties shows that the slip body VT₀₇ differs from the MZTs₀₇ and VTs₅₀₇ bodies by considerably lower values of P_{k2} and dynamic plasticity.

TABLE 5. Rheological Properties of Slip Bodies

Sample	Constrained dynamical yield stress P_{k2} , Pa	Lowest plastic viscosity $\eta_m^x \times 10^{-2}$, Pa · sec	Dynamic plasticity $\Psi \times 10^4$, sec ⁻¹
MZTs ₀₇	224.0	0.54	4.16
VTs ₅₀₇	277.5	0.47	5.87
VT ₀₇	79.3	0.87	0.91

Testing showed the correlation between the indicated parameters of coagulation structure formation and casting technology (Table 6) and the improvement of the rheological properties of the VT₀₇ body compared with MZTs₀₇ and VTs₅₀₇ with the same moisture content is associated with relatively higher flowability, and the higher filtration is confirmed by the considerably larger casting per unit time (factor of 1.6 – 1.7 in 10 min and 1.7 in 1.5 h).

STRUCTURE FORMATION DURING FIRING OF CERAMIC BODIES

When a ceramic made from the bodies studied here is fired a structure characterized by the presence of crystalline phases of quartz, feldspars, mullite and a glass phase (see Fig. 1) is formed.

After firing at maximum temperature 1000°C a very small amount of mullite is formed, the content of quartz and microcline is high and the amount of orthoclase and albite is significantly lower than in the initial composition. After the kilning temperature is increased to 1100°C a glass phase de-

TABLE 6. Technological Properties of Bodies for Casting Sanitary Ware Ceramics

Indicator	Body code		
	VT ₀₇	MZTs ₀₇	VTs ₅₀₇
Moisture content, %	28.5	29.6	29.2
Density, g/cm ³	1.80	1.77	1.77
Engler viscometer, flowability, sec:			
in 30 sec	5.0	6.0	6.0
in 30 min	7.0	9.0	8.0
Thickening factor	1.4	1.5	1.3
Casting in 10 min, g	70.7	44.1	41.2
Moisture content of casting, %	17.5	18.4	17.7
Crock buildup in 1 h 30 min, mm	10.0	7.0	6.0

velops and considerable mullite formation and a sharp drop of the microcline content occur.

At the final firing temperature in a tunnel furnace at 1220°C the amount and degree of morphological perfection of the mullite crystals distributed in the glass phase increase significantly.

CONCLUSIONS

1. The adoption in the production of ceramics for sanitary ware of the technology of pressure casting in polymer molds requires bodies that secure definite rheological and filtration properties of the slip at the molding stage and high degree of sintering of porcelain during firing.

2. The VT₀₇ body for pressure casting in polymer molds is distinguished from the MZTs₀₇ and VTs₅₀₇ bodies by a smaller effective specific surface and lower hydrophilicity of the components, which is mainly determined by the low content (50.5 versus 65.4 – 67.0%) of clayey components and change of their quantitative ratios with non-clayey materials (inert and fusing) to 1:1 versus 2:1.

3. The differences in the composition, dispersity, surface properties and hydrophylicity of the raw material components determine the characteristics of the coagulation structure formation of slip bodies with decreasing filtration properties, which is especially important when using the pressure casting technology.

4. The chemical-mineralogical composition of VT type bodies makes it possible to address comprehensively the optimization of the slip parameters for coagulation structure formation of a water dispersion system and the porcelain

structure formed during firing with glass and crystalline phases developed to the required degree.

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